이학석사 학위논문

Poly(3,4-dimethyl-5-vinylthiazolium)s catalyzed reactions

3,4-다이메틸-5-바이닐싸이아졸리움 고분자 촉매를 이용한 반응들

2015 년 8 월

서울대학교 대학원

화학부 무기화학전공

정 준 용

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By

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A Thesis for M.S. Degree

In Inorganic Chemistry

06-2015

Department of Chemistry

Graduate School

Seoul National University

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지도 교수 정 영 근

이 논문을 이학석사 학위논문으로 제출함
2015 년 6 월

서울대학교 대학원
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정준용

정준용의 이학석사 학위논문을 인준함
2015 년 6 월

위 원 장 _____ (인)

부위원장 _____ (인)

위 원 _____ (인)

Abstract

Poly(3,4-dimethyl-5-vinylthiazolium)s were synthesized from 3,4-dimethyl-5-vinylthiazole via free radical polymerization. It examined as polymer precatalysts in the presence of DBU for the thioesterification of aldehydes with thiols and for the thiol-ene click reaction of styrene with thiols. The poly(5-vinylthiazolium)s had excellent catalytic activity and could be reused more then three times without loss of activity.

Keywords: Polymer precatalysts, Poly(vinylthiazolium)s, Thioesterification, Thiol-ene click reaction, Recycling catalyst

Contents

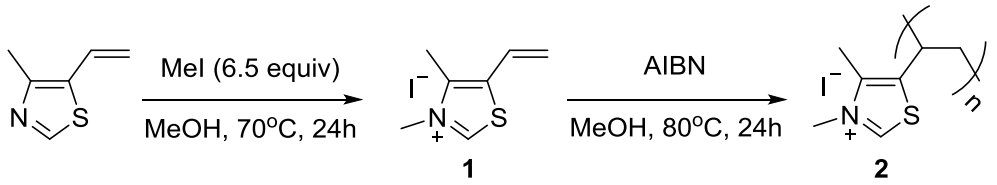
Introduction

Recently, organocatalysts related to green chemistry have attracted much attention.[1] One of the advantages of organocatalysts is that the catalytic reaction does not require a metal catalyst. However, most organic syntheses need a large amount of the organic catalysts and are performed in a homogeneous medium; hence, recovery and reuse of the catalysts is often infeasible. To overcome these obstacles, heterogenization of organocatalysts over to organic polymers or mesoporous materials were recently reported.[2] However, most of them suffered from relatively low yields and poor recyclability, presumably due to the poor stability or degradation of the catalysts in the reaction conditions. We recently developed a highly efficient, recyclable polymer-based organocatalytic system, i.e., poly(4-vinylimidazolium)s,[3] which shows high catalytic activity for benzoin condensation and cycloaddition of CO_2 to epoxides. These polymeric catalysts were successfully recovered and reused over several cycles without any loss of performance. Our interest in poly(vinylimidazolium)s led us to study poly(vinylthiazolium)s. Thiazoles have been widely studied in materials science;[4] however, to the best of our knowledge, there is no report on the synthesis and chemistry of poly(vinylthiazolium)s. Therefore, we decided to study the polymerization of 4-methyl-5-vinylthiazole because it is commercially available and its polymerization to poly(4-methyl-5-

vinylthiazole)s has not yet been reported. We also studied the use of poly(vinylthiazolium)s as a precatalyst for the thioesterification of aldehydes with thiols, because direct thioesterification of aldehydes has received relatively little attention compared to direct aldehyde-to-ester conversions.[5] Thioesters are wide spread in biochemistry[6] and versatile building blocks for the construction of various natural products.[7] Many useful synthetic routes have been developed.[8] However, only fewer studies on NHC-catalyzed thioesterification have been reported so far.[9] Herein, we communicate the synthesis of poly(vinylthiazolium)s from 3,4-dimethyl-5-vinylthiazolium and its use as a precatalyst for thioesterification of aldehyde and alkyl thiols. In 1989, Tsuda et al. reported thiazolium salt polymers.[10] According to their report, N-methyl-4-vinylphenylthiazolium iodide could not be not polymerized by radical initiators. Therefore, 4-vinylphenylthiazole was polymerized, and the resultant polythiazole was quaternized using methyl iodide. The degree of quaternization was calculated via elemental analysis of iodine. After we found the activity of poly(vinylthiazolium)s using thioesterification, we characterized deference with poly(vinylimidazolium)s. In 2015 Arun K. Sinha et al reported carbon–heteroatom (C-S) bonds reaction (thiol- ene click reaction) which did not studied using non metalic catalyst can synthesized via NHC-catalyst in the neutral ionic liquid [hmim]Br.[11] Poly(vinylthiazolium)s have a great effect in this reaction.

Results and Discussion

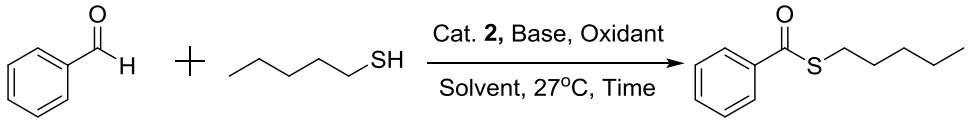
We synthesized poly(vinylthiazolium)s from 3,4-dimethyl-5-vinylthiazol-3-ium using a radical initiator, i.e., AIBN (Scheme 1).



Scheme 1. Synthesize of poly(vinylthiazolium)s

3,4-Dimethyl-5-vinylthiazol-3-ium **(1)** was prepared via the reaction of 4-methyl-5-vinylthiazole, which is commercially available, with methyl iodide. The reaction of 4-methyl-5-vinylthiazole with methyl iodide afforded 3,4-dimethyl-5-vinylthiazol-3-ium in 87 % yield. Polymerization of **1** in the presence of AIBN afforded poly(3,4-dimethyl-5-vinylthiazol-3-ium)s, **2**, which is the organocatalyst precursor, in various yields depending on the reaction conditions (see Supporting Information). Broad ^{1}H NMR signals were observed, as expected for a high molecular weight polymer. The polymer was slightly soluble in DMSO, DMF, and water at room temperature, but insoluble in other polar solvents including chloroform, dichloromethane, and acetone. The weight average molecular weight (Mw) of **2** was ~42700, as determined using light scattering experiments.[12]

Table 1. Screening of optimal reaction comditions[a]



Entry	Cat. **2** (mol%)	Base (mol%)	Oxidant	Solvent	Time (h)	Yield (%)
1	10	DBU (10)	Phenazine	DMSO	24	90
2	10	DBU (10)	Azobenzene	DMSO	24	91
3	10	DBU (10)	MnO_2	DMSO	24	38
4	10	DBU (10)	O_2	DMSO	24	7
5	10	TEA (10)	Phenazine	DMSO	24	69
6	10	DBU (10)	Phenazine	DMF	24	92
7	7	DBU (7)	Phenazine	DMF	24	93
8	5	DBU (5)	Phenazine	DMF	24	97
9	3	DBU (3)	Phenazine	DMF	24	86
10	5	DBU (5)	Phenazine	DMF	12	95
11	5	DBU (5)	Phenazine	DMF	9	92
12	4	DBU (4)	Phenazine	DMF	12	97
13	4	DBU (4)	Azobenzene	DMF	12	11
14[b]	4	DBU (4)	Phenazine	DMF	12	50

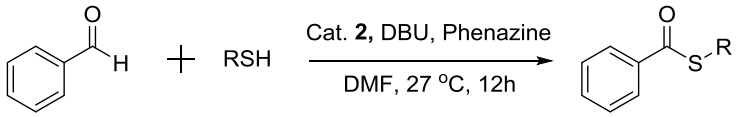
[a]Conditions: benzaldehyde (1 mmol), 1-pentanethiol (1.1 equiv), Oxidant (1.2 equiv), Solvent (1 mL), [b]Cat. **1** used

As a model reaction for thioesterification, we initially examined the reaction of benzaldehyde with 1-pentanthiol in the presence of **2** (10 mol%), an oxidant (1.2 equiv), and DBU (10 mol%) in DMSO at room temperature for 24 h (Table 1). The use of oxidants such as phenazine, MnO_2, and O_2 afforded the corresponding thioester in 90%, 38%, and 7% yields, respectively (entries 1 ~ 4). However, t-butyl hydroperoxide, 2-iodobenzoic acid, potassium persulfate,

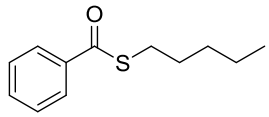
diethyl azodicarboxylate, 4-phenyl-1,2,4-triazole-3,5-dione, and (diaccetoxyiodoe)benzene oxidants gave only trace amounts of the corresponding thioester (not shown in Table 1). The use of azobenzene as an oxidant resulted in a considerable amount of product; however, purification of the product was difficult because its polarity is similar to that of azobenzene. Replacement of DBU with triethylamine in the presence of poly(4-methyl-5-vinylthiazolium)s and phenazine led to a lower isolated yield (69%) (entry 5), while changing the reaction solvent from DMSO to DMF gave a better yield of 92% (entry 6). The amount of catalyst used also influenced the yield of the reaction (entries 6 ~ 9). The yield of the reaction was slightly dependent on the reaction time (entries 9 ~ 11). The optimum reaction conditions were as follows: 4 mol% **2**, 4 mol% DBU, 1.2 equiv phenazine, 1 mL DMF, room temperature, and 12 h reaction time (entry 12). Moreover, the catalytic activity of **2** was higher than that of **1** (entry 14; 50%). Several years ago, Murata et al, reported the use of 3-butyl-4-methylthiazolium bromide as a catalyst for the reaction of benzaldehydes with azobenzene in dichloromethane containing octanethiol and Et_3N.[9a] They isolated the corresponding S-octyl thiobenzoates with a concomitant formation of hydrazide derivatives.

Using the optimized reaction conditions, the catalytic activity of **2** was investigated for the reaction of benzaldehyde with a diverse variety of thiols (Table 2). Various alkyl thiols containing hydroxyl, alkene, or aryl groups afforded high to excellent yields of the corresponding thioesters (3ab, 3ac, 3ag, 3ah, and 3ak). In the case

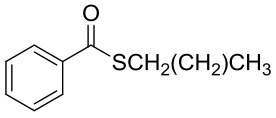
Table 2. Thioesterification of thiols[a]



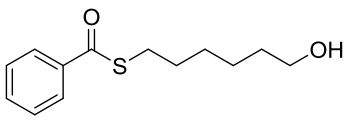
3



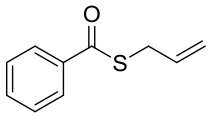
3aa, 97%[b]



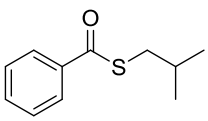
3ab, 96%



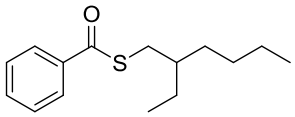
3ac[c], 80%



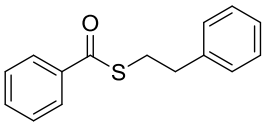
3ad[d], 83%



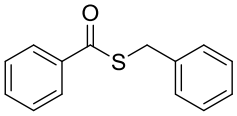
3ae, 89%



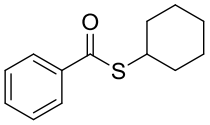
3af, 76%



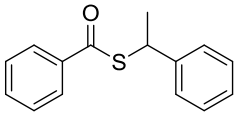
3ag, 88%



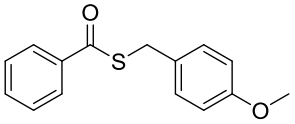
3ah, 90%



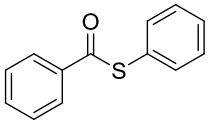
3ai, 87%



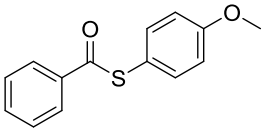
3aj, 98%



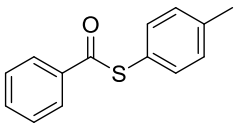
3ak, 90%



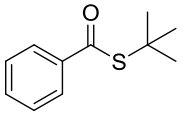
3al[e], 79% (15%)[f]



3am[e], 56% (25%)[f]



3an[e], 51% (28%)[f]



3ao[e], 74% (23%)[f]

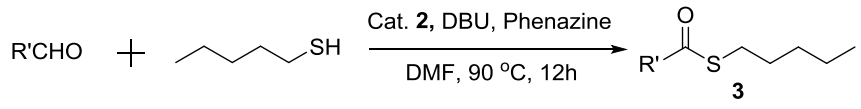
[a]Conditions: benzaldehyde (1 mmol), thiols (1.1 equiv), Cat. **2** (4 mol%), DBU (4 mol%), Phenazine (1.2 equiv), DMF (1mL). [b]Isolated yield. [c]Selectivity of thioesterification and esterification (98 : 2) [d]Conditions: Cat. **2** (7 mol%), DBU (7 mol%), [e]Conditions: Cat. **2** (10 mol%), DBU (10 mol%), 40 °C, 24h, [f]Cat. **2** (4 mol%) used

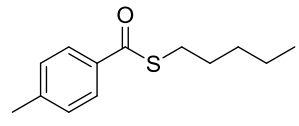
of allyl thiol, the yield was highly sensitive to the amount of 2; 4 mol% 2 generated a yield of 32%, while 7 mol% 2 generated a yield of 83%. For 6-mercaptohexan-1-ol (3ac), two reaction products could be produced because of the presence of two potential reaction sites.[13] However, excellent thia-selectivity over oxa-slectivity

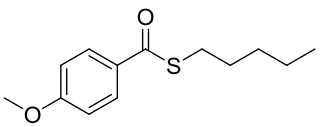
(98:2) was observed. Secondary alkyl thiols (3ai and 3aj) also gave excellent yields of thioesters. For aryl thiols and t-butyl thiol (3al ~3ao), poor yields (15 ~ 28%) were obtained in the presence of 4 mol% **2**. However, the yields dramatically increased to 51 ~ 79% in the presence of 10 mol% **2** at 40℃. Therefore, the catalytic system is quite effective for the reaction of benzaldehyde with alkyl and aryl thiols.

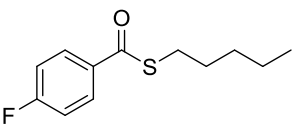
We next investigated the reaction of various aldehydes with 1-pentanthiol (Table 3). Most aryl aldehydes were good substrates at room temperature; however, aryl aldehydes with halo or nitro substituents did not provide high yields at room temperature. Therefore, for these substrates, we altered the reaction temperature and determined that the optimal temperature was 90 ℃ (see Supporting Information). Aromatic as well as aliphatic aldehydes react with 1-pentathiol using this procedure. A wide range of aromatic aldehydes bearing both electron-donating and electron-withdrawing groups could be used regardless of the positions of their substituents to give the corresponding thioesters in high yields (3ba, 3fa, 3ha ~3ma, and 3pa) except nitrobenzaldehydes (3ga and 3na). In particular, 2-chloro-5-nitrobenzaldehyde (3na), which has two electron-withdrawing substituents on the aromatic ring, gave a poor yield (30%). Cyclohexane carbaldehyde (3oa), which is an example of an unactivated aldehyde, gave a good yield of thioester (85%). Heteroaromatic aldehydes such as furan-2-carbaldehyde and picolinaldehyde (3qa and 3ra) also gave high yields (77% and 69%, respectively). Alkyl aldehydes with phenyl groups (3sa and

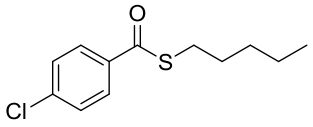
Table 3. Thioesterification of aldehydes[a]

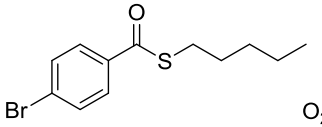


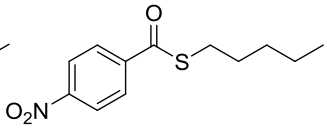

3ba, 98%[b] (93%)[c]

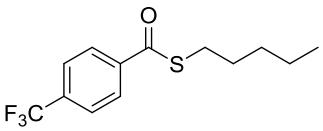

3ca, 75%

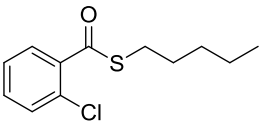

3da, 89%

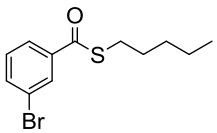

3ea, 86%

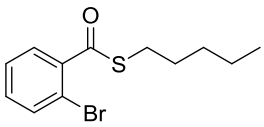

3fa, 84%

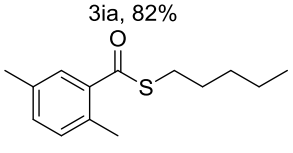

3ga, 48%

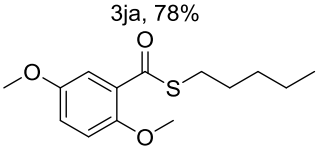

3ha, 88%

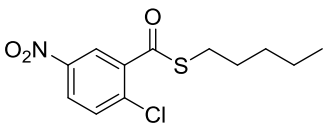

3ia, 82%

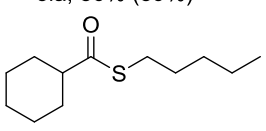

3ja, 78%

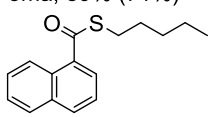

3ka, 85%

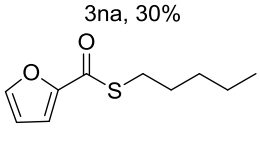

3la, 86% (89%)[c]

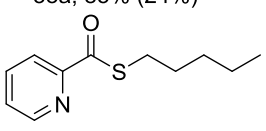

3ma, 89% (71%)[c]

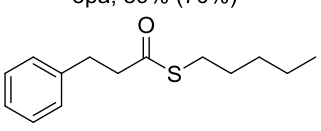

3na, 30%

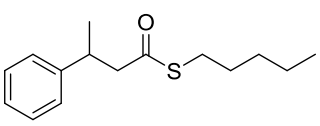

3oa, 85% (24%)[c]

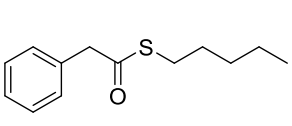

3pa, 89% (70%)[c]

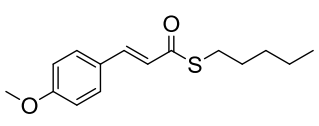

3qa, 77%


3ra, 69%


3sa, 86%


3ta, 88%


3ua[d], 43%


3va[d], 47%

[a]Conditions: aldehydes (1 mmol), 1-pentanethiol (1.1 equiv), Cat. **2** (4 mol%), DBU (4 mol%), Phenazine (1.2 equiv), DMF (1mL). [b]Isolated yield. [c]At room temperature. [d]Conditions: Cat. **2** (10 mol%), DBU (10 mol%), 24h

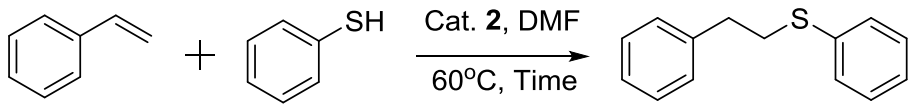
3ta) were good substrates (86% and 88% yield, respectively).

However, for 2-phenylacetaldehyde and 3-(4-methoxyphenyl)acrylaldehyde (3ua and 3va), a longer reaction time (24 h) was needed to give moderate yields (43% and 47%, respectively).

The reusability of **2** was also examined. For the recycling test, 10 mol% **2** was used. The polymer catalyst was recovered by the addition of excess acetone in the reaction mixture. The precipitate was filtered and washed with acetone and dried. The catalyst was successfully reused without loss of performance over three cycles (89%, 87%, and 90% yields, respectively); however, the yield abruptly dropped to 42% during the fourth cycle. Because only small amount of **2** was used as the catalyst, the loss during separation was very significant. Therefore, a better recovery process is needed.

Increase turnover number of **2**, we examined the thiol-ene click reaction of styrene with benzenethiol, **2** (5 mol%), in DMF at 60℃ for 60 min (Table 4) because of this reaction use catalyst only. The amount of catalyst used influenced the yield of the reaction (entries 1 ~ 4). When we initialy examined this reaction, schlenk flask was flame-dried and charged N_2 gas to make inert condition. Acroding to the Arun K. Sinha study, 4-vinylbiphenyl with benzenethiol synthesized in netural ionic liquid. So, we thought vinyl group and thiol can make bonding in non inert condition (entry 5). The optimum reaction conditions were as follows: 5 mol% **2**, 1 mL DMF, 60℃, and 90 min reaction time in air condition (entry 6). Moreover, the catalytic activity of **2** was higher than that of poly(imidazolium)s

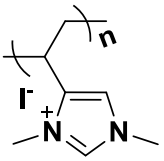
Table 4. Thiol + ene reaction of styrene with Benzenethiol[a]



1a **2b**

Entry	Cat. 2 (mol%)	Time (min)	Yield (%)
1	5	60	82
2	3	60	56
3	1	60	53
4	0	60	0
5[b]	5	60	93
6[b]	5	90	98
7[c]	5	90	0

[a]Conditions: **1a** (1 mmol), **2b** (1mmol), 60°C, DMF (1mL) [b]In air conditions. [c]use Cat. **3**



Cat. **3**

cata lyst (entry7). The recycling test of 2 was also examined 10 mol% 2 was used. The catalyst was successfully reused without loss of performance over four cycles (86%, 87%, 84% and 81% yields, respectively) used the same method as thioesterification.

Conclusion

In conclusion, we developed a polymer-based organocatalytic system **(2)** via polymerization of 3,4-dimethyl-5-vinylthiazolium; this system showed high catalytic activity for thioesterification of aldehydes with thiols and thiol-ene click reaction. Precatalyst **2** provided higher catalytic activity than the monomeric analog **(1)** and could be reused three times without loss of activity. Precatalyst **2** has great potential given that a better recovery process is developed. Further investigations of applicability of the polymer-based thiazolium system for other reactions are on-going in our laboratory.

Experimental Section

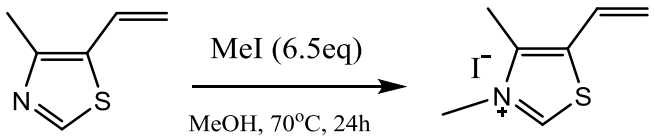
General remarks.

All solvents were obtained by passing through activated alumina columns of solvent purification systems from Glass Contour. n-Hexanes and ethyl acetate were used without further purification. Reagents were purchased from Sigma-Aldrich, Alfa Aesar, Acros, and TCI and were used as received. DMF were used as a solvent. Azobisbutyronitrile (AIBN) was purchased and recrystallized from methanol before use. Reactions were carried out in a flame -dried glassware equipped with a stirring bar and capped with a rubber septum under N_2, unless otherwise indicated. Elevated temperatures were maintained in thermostat-controlled oil baths. The TLC plate was carried out on 0.25 mm E. Merck silica gel plates (60F-254) visualized by UV-light (254 nm) and treatment with acidic p-anisaldehyde and $KMnO_4$ stain followed by gentle heating. Workup procedures were done in air. Flash chromatography was carried out on Merck 60 silica gel (230 – 400 mesh). IR spectra were measured on a Thermo Scientific Nicolet 6700 spectrometer. ^1H and ^{13}C NMR spectra were recorded with Varian spectrometer (400 MHz) spectrometer. ^1H NMR spectra were referenced to residual TMS (0 ppm), methanol (solvent reference, 3.31), DMSO (solvent reference, 2.50 ppm) and reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, ddd = doublet of doublet of doublets, dt = doublets of triplets, td =

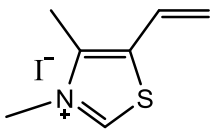
triplet of doublets, qd = quertet of doublets, br s = broad singlet, m = multiplet). Chemical shifts of the ^{13}C NMR spectra were measured relative to $CDCl_3$ (77.16 ppm). Mass spectral data were obtained from the Korea Basic Science Institute (Daegu) on a Jeol JMS 700 high resolution mass spectrometer. Static light scattering (SLS) measurements were measured by Dynamic Light Scattering Spectrophotometer (DLS-7000) at National Instrumentation Center for Environmental Management (NICEM), College of Agriculture and Life Sciences, Seoul National University, Korea.

Preparation and Characterization of Precatalysts 1 and 2

A. Synthesis of monomer **1**.

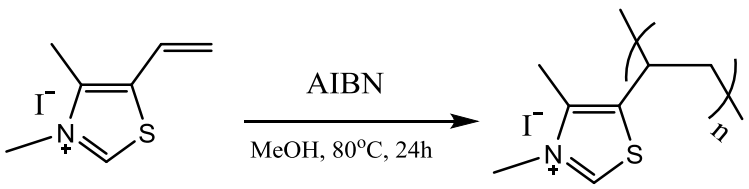


4-Methyl-5-vinythiazole (0.12 g, 1 mmol), iodomethane (0.2ml, 6.5 mmol) and methanol (8 mL) were added to a Schlenk flask. The reaction mixture was stirred at 70℃ for 24 hours. The solvent was evaporated from the filtrate. Then, the reaction mixture was purified by a flash chromatography on a silica gel column eluting with dichloromethane/methanol (v/v, 10:1).



3,4-Dimethyl-5-vinylthiazolium iodide: **^{1}H NMR (400 MHz, CD_3OD)** δ 7.02 (dd, J = 17.2, 11.1 Hz, 1H), 5.94 (d, J = 17.3 Hz, 1H), 5.67 (d, J = 11.1 Hz, 1H), 4.15 (s, 3H), 3.31 – 3.29 (m, 1H), 2.58 (s, 3H) ppm. **^{13}C NMR (101 MHz, CD_3OD)** δ 124.09, 120.69, 48.22, 48.01, 47.80, 47.59, 47.37, 47.16, 46.95, 40.01, 10.52 ppm. **HRMS (FAB)** calc. for [$C_7H_{10}NS$]: 140.2234, found: 140.2294. , pale yellow solid; yield, 87%.

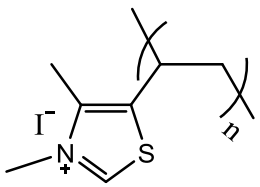
B. Synthesis of polymer catalyst **2**.



In a typical experiment, a 10 mL Schlenk flask was flame-dried and charged with 3 mmol of **1**, 0.012 mmol of AIBN and 3 mL of methanol. The Schlenk tube was subjected to three freeze-pump-thaw cycles and placed in a thermostatted oil bath previously maintained at 80℃. The polymerization reaction was quenched after 24h by a sudden cooling with liquid nitrogen. The resulting poly(3,4-dimethyl-5-vinylthiazolium) salt **2** was isolated by precipitation in acetone solution. After drying under vacuum, **2** was obtained as a light green powder. Yield: 39%.

Optimization of the polymerization of 3,4−dimethyl−5−vinylthiazolium iodide

Entry	AIBN (mol%)	Solvent	Temp (^{o}C)	Time (h)	Yield (%)
1	0.4	MeOH (3)	80	11	15
2	1	MeOH (3)	80	11	15
3	0.4	MeOH (3)	80	24	39
4	0.4	MeOH (3)	80	48	42
5	0.4	MeOH (3)	60	24	14
6	0.4	DMF+MeOH (2.5 + 0.5)	80	24	28
7	0.4	DMF+MeOH (2 + 1)	80	24	38
8	0.4	DMF+MeOH (1.5+ 1.5)	80	24	44
9	0.4	MeOH (2)	80	24	40
10	0.4	MeOH (2)	80	48	51
11	0.4	MeOH (2)	80	72	53



Poly(3,4−dimethyl−5−vinylthiazolium) iodide: **^{1}H NMR (400 MHz, DMSO)** δ 10.12 (s, 1H), 4.15 (s, 3H), 2.55 (s, 3H) ppm. **^{13}C NMR (101 MHz, DMSO)** δ 49.04, 40.60, 40.42, 40.28, 39.86, 39.59, 39.45, 31.29 ppm. Mw = 4.272 x 104 by SLS, dec. temp.: 267 oC.

Characterization of 2 by Static Light Scattering (SLS)

A. Sample Preperation and Measurement.

Absolute molecular weight (MW) value was measured by SLS. The solvent, DMSO, was filterd by using a 0.2 μm PVDF filter for removing dust before use. The initial concentration of catalyst solution was 25 mg/25 mL (1 g/L). The solutions of **2** were prepared in a pre-cleaned vial with ultra sonnication for 6 h to get a homogeneous solution. Then the high concentration (1 g/L) was diluted to 0.25, 0.3, 0.35, 0.4, 0.45, 0.5 g/L with adding DMSO in pre-cleaned vials. Then, the solutions with various polymer concentrations were filtered again through 0.2 μm PVDF filters and ultra sonicated overnight to stabilize the solutions before SLS measurements. The light scattering measurements were carried out at 25℃. Measurements were taken using a DLS-7000 apparatus, a commercial spectrometer from Otsuka electronics. The light source was argon ion laser operated at a power of 75 mW and a wave length of the 488 nm which was focused on the sample cell. The scattered angles were taken from 40 to 130 degree, 10 degree of intervals for each sample. The refractive index increment (dn/dc) was measured on an Otsuka electronics DRM-1021 to calculate the weight average molecular weight for catalyst.

B. Zimm plot by Static Light Scattering.

The second virial coefficient, A2, obtained from the SLS measurement, denotes the degree of the polymer–solvent interaction

in the dilute solution. Figure S1 shows the Zimm plot of poly(3,4-dimethyl-5-vinylthiazole) /DMSO solution at 25℃. The A2 is about -1.683×10^{-1} cm^3 mol g^{-2} at 14.1 ℃. The negative A2 values are still found at the whole range of the measuring temperature in this work. The absolute Mw value was determined by SLS and the value was 4.272×10^4.

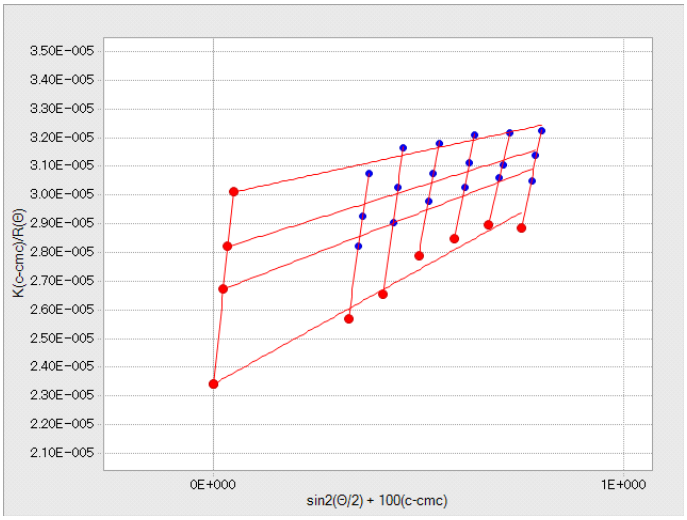


Figure S1. Zimm plot of Poly(3,4-dimethyl-5-vinylthiazolium) iodide/DMSO solution at 25℃

Measurement condition	
dn/dc (ml/g)	2.7423
Solvent refractive index	1.4790
Temperature (℃)	25.0
Ph 1	Open
Ph 2	Slit

ND Filter	5%
Angle (°)	70, 80, 90, 100, 110, 120
Concentration (mg/ml)	0.25, 0.35, 0.5

Table S1. Measurement conditions of SLS

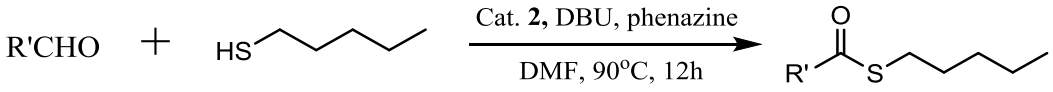
Procedure for the synthesis of Thioesterification

A. Procedure for the Synthesis of Thioesterification by using Various Thiols

Reactions were performed in a tube schlenk equipped with a stirring bar and capped with a rubber cap and the followings were placed in the tube in order: 4 mol% of catalyst **2** (10 mg, 0.04 mmol), 4 mol% of DBU (6 mg,0.04 mmol), benzaldehyde (0.11 g, 1 mmol), phenazine (0.22g, 1.2 mmol), various thiols (1.1 mmol) and 1mL of DMF at room termperture for 12 hours. The reaction mixture was added in acetone and catalysts were filtered and filtrate was concentrated under reduced pressure. Purification by flash chromatography on silica gel with n-hexane and ethyl acetate afford thioester. The thioester products were characterized by ^{1}H NMR, ^{13}C NMR, IR and HRMS.

B. Procedure for the Synthesis of Thioesterification by using

Various Aldehydes



Optimization of the reaction of various aldehydes

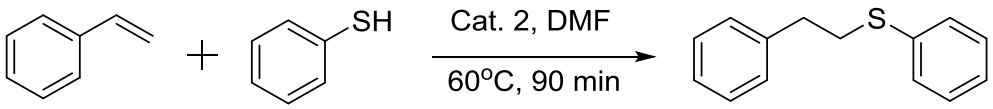
Entry	Cat. **2** (mol%)	DBU (mol%)	Temp (°C)	Yield (%)
1	4	4	27	43
2	7	7	27	69
3	4	4	50	49
4	4	4	70	68
5	4	4	90	86
6	4	4	110	81

Reactions were performed in a tube schlenk equipped with a stirring bar and capped with a rubber cap and the followings were placed in the tube in order: 4 mol% of catalyst **2** (10 mg, 0.04 mmol), 4 mol% of DBU (6 mg,0.04 mmol), 1-pentanethiol (0.11 g, 1.1 mmol), phenazine (0.22g, 1.2 mmol), various aldehydes (1 mmol) and 1mL of DMF at 90℃ for 12 hours. The reaction mixture was added in acetone and catalysts were filtered and filtrate was concentrated under reduced pressure. Purification by flash chromatography on silica gel with n-hexane and ethyl acetate afford thioester. The thioester products were characterized by ^{1}H NMR, ^{13}C NMR, IR and HRMS.

Recycling test

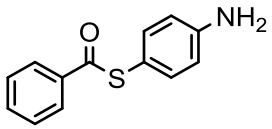
A Schlenk tube was charged with 1 mmol of benzaldehyde (106 mg), 1.1 mmol pentanethiol (116 mg), 1.2 mmol phenazine (220 mg), 10 mol% of catalyst (26 mg, 0.1 mmol), 10 mol% of DBU (15 mg,0.1 mmol) and 1 mL of DMF. After stirring for 12 h at room temperature, the polymer catalyst was successfully recovered by precipitation from the reaction mixture by addition of acetone. The solvents were evaporated from the filtrate, and the residue was purified by flash column chromatograpy. The recovered catalyst were used with 10 mol% of DBU and 1 mL of DMF. The catalytic performance of poly(NHC) was well maintained during the three recycling with 87–91% isolated yields.

Procedure for the synthesis of Thiol–ene click reaction

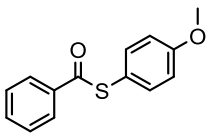


Reactions were performed in a tube schlenk equipped with a stirring bar and capped with a rubber cap and the followings were placed in the tube in order: 5 mol% of catalyst **2** (13 mg, 0.05 mmol), styrene (0.10 g, 1 mmol), benzenethiol (0.11g, 1 mmol) and 1mL of DMF at 60℃ for 90 min. The reaction mixture was added in acetone and catalysts were filtered and filtrate was concentrated under reduced pressure. Purification by flash chromatography on silica gel with n–hexane and ethyl acetate afford carbon–sulfer (C–S) bonds.

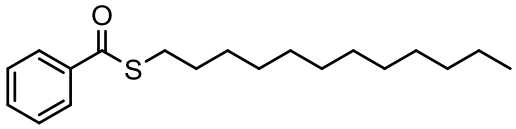
^{1}H NMR, ^{13}C NMR, IR, HRMS and IR data of reaction products:



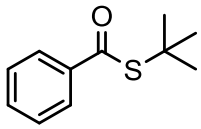
S−(4−aminophenyl) benzothioate: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.01 (d, J = 7.8 Hz, 2 H), 7.57 (d, J = 7.4 Hz, 1 H), 7.46 (t, J = 7.7 Hz, 2 H), 7.28 – 7.23 (m, 2 H), 6.74 – 6.69 (m, 2 H), 3.88 (s, 2 H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 191.9, 148.1, 136.8, 136.5, 133.5, 128.7, 127.5, 115.7 ppm. **HRMS (EI)** calc. for [$C_{13}H_{11}NOS$]: 229.0561, found: 229.0563; **IR (neat)**: 1664 cm^{-1} (C=O); yellow solid; **MP** 101℃.



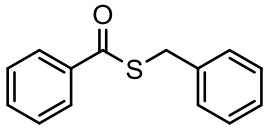
S−(4−methoxyphenyl) benzothioate: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.05 – 7.99 (m, 2 H), 7.59 (s, 1 H), 7.47 (t, J = 7.7 Hz, 2 H), 7.41 (d, J = 8.2 Hz, 2 H), 6.98 (d, J = 8.2 Hz, 2 H), 3.83 (d, J = 0.7 Hz, 3 H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 191.1, 160.8, 136.7, 133.6, 128.8, 127.5, 117.9, 115.0, 55.4 ppm. **HRMS (EI)** calc. for [$C_{14}H_{12}O_2S$]: 224.0558, found: 224.0555; **IR (neat)**: 1670 cm^{-1} (C=O); white solid; **MP** 98℃.



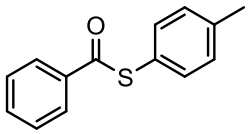
S−dodecyl benzothioate: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.00 – 7.91 (m, 2 H), 7.52 – 7.45 (m, 1 H), 7.38 (t, J = 7.7 Hz, 2 H), 3.04 (t, J = 7.4 Hz, 2 H), 1.66 (dd, J = 14.7, 7.2 Hz, 2 H), 1.43 – 1.37 (m, 2 H), 1.29 – 1.26 (m, 16 H), 0.88 (t, J = 6.8 Hz, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 191.6, 137.2, 133.0, 128.4, 127.1, 31.9, 29.8, 29.7 (2), 29.6 (2), 29.5, 29.2, 29.0, 22.7, 14.1 ppm. **HRMS (EI)** calc. for [$C_{19}H_{30}OS$]: 306.2017, found: 306.2015; **IR (neat)**: 1664 cm^{-1} (C=O); colorless oil.



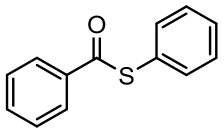
S−(tert−butyl) benzothioate: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.94 – 7.89 (m, 2H), 7.51 (d, J = 7.4 Hz, 1 H), 7.43 – 7.38 (m, 2 H), 1.58 (s, 9 H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 192.9, 138.3, 133.0, 128.5, 127.0, 48.2, 30.1 ppm. **HRMS (EI)** calc. for [$C_{11}H_{14}OS$]: 194.0765, found: 194.0765; **IR (neat)**: 1656 cm^{-1} (C=O); colorless oil.



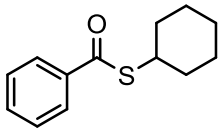
S-benzyl benzothioate: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.96 (dd, J = 8.3, 1.2 Hz, 2 H), 7.56 – 7.50 (m, 1 H), 7.45 – 7.34 (m, 4 H), 7.30 (dd, J = 7.9, 6.6 Hz, 2 H), 7.26 – 7.21 (m, 1 H), 4.31 (s, 2 H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 191.3, 137.5, 136.8, 133.5, 129.0, 128.7, 127.4, 33.4 ppm. **HRMS (EI)** calc. for [$C_{14}H_{12}OS$]: 228.0609, found: 228.0607; **IR (neat)**: 1659 cm^{-1} (C=O); colorless oil.



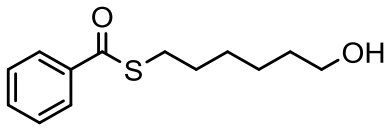
S-(p-tolyl) benzothioate: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.02 (d, J = 8.1 Hz, 2H), 7.57 (t, J = 6.8 Hz, 1H), 7.46 (t, J = 7.0 Hz, 2H), 7.39 (d, J = 6.8 Hz, 2H), 7.25 (d, J = 7.7 Hz, 2H), 2.39 (s, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 190.6, 139.8, 136.7, 135.1, 133.6, 130.1, 128.8, 127.5, 123.8, 21.4 ppm. **HRMS (EI)** calc. for [$C_{14}H_{12}OS$]: 228.0609, found: 228.0605; **IR (neat)**: 1666 cm^{-1} (C=O); white solid; **MP** 70℃.



S−phenyl benzothioate: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.05 – 7.98 (m, 2 H), 7.60 – 7.56 (m, 1 H), 7.53 – 7.42 (m, 7 H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 190.2, 136.6, 135.1, 133.7, 129.6, 129.3, 128.8, 127.4 ppm. **HRMS (EI)** calc. for [$C_{13}H_{10}OS$]: 214.0452, found: 214.0454; **IR (neat)**: 1664 cm^{-1} (C=O); white solid; **MP** 57℃.

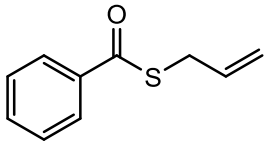


S−cyclohexyl benzothioate: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.98 – 7.91 (m, 2H), 7.51 (tdd, J = 3.9, 2.6, 1.3 Hz, 1H), 7.40 (ddd, J = 7.6, 4.1, 1.2 Hz, 2H), 3.73 (d, J = 6.2 Hz, 1H), 2.02 – 2.00 (m, 2H), 1.77 – 1.70 (m, 2H), 1.61 (m, 1H), 1.49 (m, 4H), 1.35 – 1.28 (m, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 191.7, 137.4, 133.1, 128.5, 127.1, 42.5, 33.1, 26.0, 25.6 ppm. **HRMS (EI)** calc. for [$C_{13}H_{16}OS$]: 220.0992, found: 220.0920; **IR (neat)**: 1658 cm^{-1} (C=O); colorless oil.

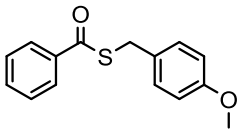


S−(6−hydroxyhexyl) benzothioate: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.96 (d, J = 7.3 Hz, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.7 Hz, 2H), 3.61 (t, J = 6.5 Hz, 2H), 3.06 (t, J = 7.3 Hz, 2H), 2.38 (s,

1H), 1.69 – 1.64 (m, 2H), 1.60 – 1.53 (m, 2H), 1.46 – 1.37 (m, 4H). ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 192.2, 137.1, 133.2, 128.5, 127.1, 62.5, 32.5, 29.5, 28.8, 28.6, 25.2 ppm. **HRMS (EI)** calc. for [$C_{13}H_{18}O_2S$]: 238.1028, found: 238.1026; **IR (neat)**: 1659 cm^{-1} (C=O); colorless oil.

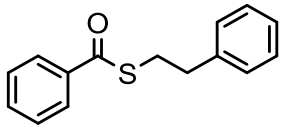


S-allyl benzothioate: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.95 (d, J = 5.9 Hz, 2H), 7.52 (t, J = 6.1 Hz, 1H), 7.40 (t, J = 6.4 Hz, 2H), 5.95 – 5.81 (m, 1H), 5.32 – 5.28 (m, 1H), 5.14 –5.11 (m, 1H), 3.71 (dd, J = 5.7, 1.0 Hz, 2H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 190.9, 136.8, 133.3, 133.0, 128.5, 127.1, 117.9, 31.7 ppm. **HRMS (EI)** calc. for [$C_{10}H_{10}OS$]: 178.0452, found: 178.0453; **IR (neat)**: 1663 cm^{-1} (C=O); colorless oil.

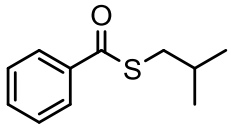


S-(4-methoxybenzyl) benzothioate: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.00 – 7.90 (m, 2.H), 7.52 (tt, J = 6.8, 1.3 Hz, 1.H), 7.44 – 7.37 (m, 2.H), 7.32 – 7.26 (m, 2.H), 6.86 – 6.80 (m, 2.H), 4.27 (d, J = 0.7 Hz,

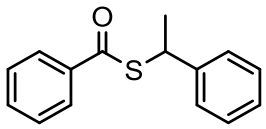
2.H), 3.76 (d, J = 1.6 Hz, 3.H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 191.5, 158.9, 136.9, 133.4, 130.1, 129.4, 128.6, 127.3, 114.1, 55.3, 32.9 ppm. **HRMS (EI)** calc. for [$C_{15}H_{14}O_2S$]: 258.0715, found: 258.0717; **IR (neat)**: 1657 cm^{-1} (C=O); colorless oil.



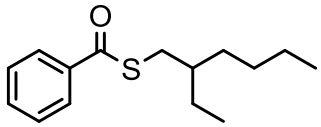
S-phenethyl benzothioate: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.99 – 7.92 (m, 2.H), 7.55 – 7.50 (m, 1.H), 7.44 – 7.38 (m, 2.H), 7.32 – 7.19 (m, 5.H), 3.33 – 3.27 (m, 2.H), 2.98 – 2.92 (m, 2.H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 191.8, 140.1, 137.1, 133.4, 128.8 (3), 127.2, 126.6, 36.0, 30.5 ppm. **HRMS (EI)** calc. for [$C_{15}H_{14}OS$]: 242.0765, found: 242.0764; **IR (neat)**: 1658 cm^{-1} (C=O); colorless oil.



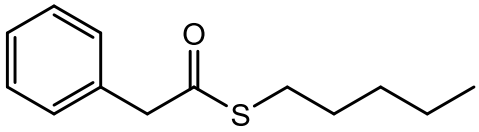
S-isobutyl benzothioate: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.98 (dt, J = 8.6, 1.7 Hz, 2H), 7.55 – 7.49 (m, 1H), 7.44 – 7.39 (m, 2H), 2.99 (d, J = 6.7 Hz, 2H), 1.94 – 1.85 (m, 1H), 1.02 (d, J = 6.7 Hz, 6H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 191.8, 137.2, 133.1, 128.5, 127.2, 37.3, 28.8, 21.9 ppm. **HRMS (EI)** calc. for [$C_{11}H_{14}OS$]: 194.0765, found: 194.0764; **IR (neat)**: 1662 cm^{-1} (C=O); colorless oil.



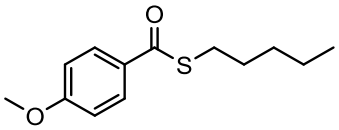
S-(1-phenylethyl) benzothioate: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.94 – 7.87 (m, 2 H), 7.48 – 7.43 (m, 1 H), 7.41 (dd, J = 4.8, 3.4 Hz, 2 H), 7.35 –7.27 (m, 4 H), 7.23 – 7.19 (m, 1 H), 5.00 – 4.92 (m, 1 H), 1.75 – 1.71 (m, 3 H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 190.9, 142.6, 136.9, 133.2, 128.5, 127.2, 43.0, 22.3 ppm. **HRMS (EI)** calc. for [C15H14OS]: 242.0765, found: 242.0763; **IR (neat)**: 1650 cm^{-1} (C=O); colorless oil.



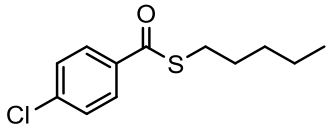
S-(2-ethylhexyl) benzothioate: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.01 – 7.95 (m, 2 H), 7.53 (dtd, J = 9.3, 2.6, 1.2 Hz, 1 H), 7.44 – 7.39 (m, 2 H), 3.15 – 3.08 (m, 2 H), 1.63 – 1.57 (m, 1 H), 1.41 – 1.29 (m, 8 H), 0.94 – 0.89 (m, 6 H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 192.0, 137.4, 133.1, 128.5, 127.2, 39.4, 33.0, 32.7, 28.9, 25.9, 23.0, 14.1, 11.0 ppm. **HRMS (EI)** calc. for [$C_{15}H_{22}OS$]: 250.1391, found: 250.1393; **IR (neat)**: 1663 cm^{-1} (C=O); colorless oil.



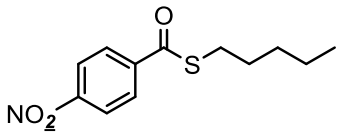
S-pentyl 2-phenylethanethioate: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.43 – 7.14 (m, 5 H), 3.80 (s, 2 H), 2.90 – 2.78 (m, 2 H), 1.59 – 1.48 (m, 2 H), 1.35 – 1.25 (m, 4 H), 0.86 (ddd, J = 6.7, 6.1, 3.5 Hz, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.6, 133.9, 129.6, 128.7, 127.4, 50.6, 31.0, 29.2, 22.2, 14.0 ppm. **HRMS (EI)** calc. for [$C_{13}H_{18}OS$]: 222.1078, found: 222.1079; **IR (neat)**: 1685 cm^{-1} (C=O); yelloew oil;



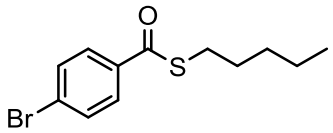
S-pentyl 4-methoxybenzothioate: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.94 (dd, J = 8.9, 0.8 Hz, 2 H), 6.94 – 6.81 (m, 2 H), 3.81 (d, J = 0.7 Hz, 3 H), 3.03 (t, J = 7.4 Hz, 2 H), 1.71 – 1.61 (m, 2 H), 1.44 – 1.31 (m, 4 H), 0.90 (t, J = 7.0 Hz, 3 H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 190.4, 163.5, 130.0, 129.2, 113.6, 55.3, 31.0, 29.4, 28.8, 22.2, 13.9 ppm. **HRMS (EI)** calc. for [$C_{13}H_{18}O_2S$]: 238.1028, found: 238.1028; **IR (neat)**: 1654 cm^{-1} (C=O); colorless oil.



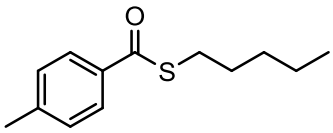
S-pentyl 4-chlorobenzothioate: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.89 (dq, J = 9.1, 2.3 Hz, 2 H), 7.42 – 7.25 (m, 2 H), 3.13 – 2.98 (m, 2 H), 1.72 – 1.59 (m, 2 H), 1.46 – 1.30 (m, 4 H), 0.96 – 0.84 (m, 3 H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 190.7, 139.5, 135.5, 128.8, 128.5, 31.1, 29.2, 22.2, 13.9 ppm. **HRMS (EI)** calc. for [$C_{12}H_{15}ClOS$]: 242.0532, found: 242.0531; **IR (neat)**: 1665 cm^{-1} (C=O); colorless oil.



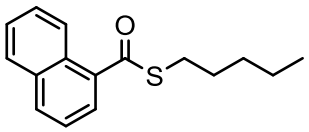
S-pentyl 4-nitrobenzothioate: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.35 – 8.23 (m, 2 H), 8.18 – 8.06 (m, 2 H), 3.11 (t, J = 7.4 Hz, 2 H), 1.74 – 1.65 (m, 2 H), 1.45 – 1.34 (m, 4 H), 0.92 (t, J = 7.1 Hz, 3 H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 190.3, 150.3, 141.7, 128.1, 123.7, 31.0, 29.5, 28.9, 22.2, 13.9 ppm. **HRMS (EI)** calc. for [$C_{12}H_{15}NO_3S$]: 253.0773, found: 253.0774; **IR (neat)**: 1663 cm^{-1} (C=O); yellow oil.



S−pentyl 4−bromobenzothioate: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92 – 7.70 (m, 2 H), 7.59 – 7.43 (m, 2 H), 3.05 (ddd, J = 8.4, 7.5, 3.2 Hz, 2 H), 1.74 – 1.58 (m, 2 H), 1.44 – 1.28 (m, 4 H), 1.00 – 0.81 (m, 3 H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 190.9, 135.9, 131.8, 128.6, 128.2, 31.1, 29.2, 22.2, 14.0 ppm. **HRMS (EI)** calc. for [$C_{12}H_{15}BrOS$]: 286.0027, found: 286.0024; **IR (neat)**: 1663 cm^{-1} (C=O); colorless oil.

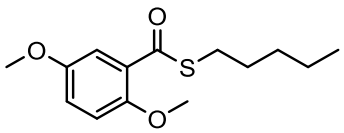


S−pentyl 4−methylbenzothioate: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.86 (d, J = 8.1 Hz, 2 H), 7.26 – 7.15 (m, 2 H), 3.03 (t, J = 7.4 Hz, 2 H), 2.36 (s, 3 H), 1.70 – 1.61 (m, 2 H), 1.43 – 1.31 (m, 4 H), 0.90 (t, J = 7.0 Hz, 3 H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 191.4, 143.8, 134.7, 129.1, 127.2, 31.1, 29.3, 28.8, 22.2, 21.5, 13.9 ppm. **HRMS (EI)** calc. for [$C_{13}H_{18}OS$]: 222.1078, found: 222.1078; **IR (neat)**: 1658 cm^{-1} (C=O); colorless oil.

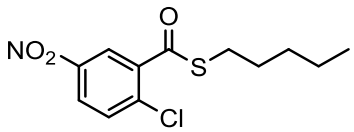


S−pentyl naphthalene−1−carbothioate: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.53 (d, J = 8.6 Hz, 1 H), 7.99 (d, J = 7.1 Hz, 1 H), 7.85 (d, J =

8.2 Hz, 1 H), 7.75 (d, J = 8.0 Hz, 1 H), 7.52 (t, J = 7.4 Hz, 1 H), 7.43 (t, J = 7.4 Hz, 1 H), 7.36 (t, J = 7.7 Hz, 1 H), 3.07 (t, J = 7.4 Hz, 2 H), 1.71 – 1.64 (m, 2 H), 1.42 – 1.28 (m, 4 H), 0.89 (t, J = 7.1 Hz, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 194.2, 135.6, 133.6, 132.5, 129.1, 128.2, 127.7, 127.4, 126.4, 125.2, 124.3, 31.1, 29.8, 29.2, 22.2, 13.9 ppm. **HRMS (EI)** calc. for [$C_{16}H_{18}OS$]: 258.1078, found: 258.1076; **IR (neat)**: 1655 cm^{-1} (C=O); colorless oil

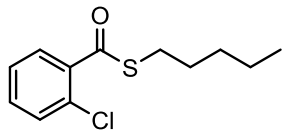


S-pentyl 2,5-dimethoxybenzothioate: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.31 (d, J = 2.9 Hz, 1 H), 6.96 (dd, J = 8.7, 2.7 Hz, 1 H), 6.87 (d, J = 9.0 Hz, 1 H), 3.83 (s, 3 H), 3.74 (s, 3 H), 2.99 (t, J = 7.4 Hz, 2 H), 1.68 – 1.61 (m, 2 H), 1.43 – 1.31 (m, 4 H), 0.90 (t, J = 6.9 Hz, 3 H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 190.8, 153.1, 152.1, 127.4, 119.3, 113.6, 56.4, 55.6, 31.1, 29.3, 29.0, 22.2, 13.8 ppm. **HRMS (EI)** calc. for [$C_{14}H_{20}O_3S$]: 268.1133, found: 268.1133; **IR (neat)**: 1663 cm^{-1} (C=O); colorless oil.

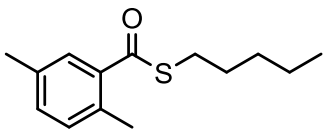


S-pentyl 2-chloro-5-nitrobenzothioate: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.48 (d, J = 2.7 Hz, 1 H), 8.28 – 8.24 (m, 1 H), 7.64 (d, J

= 8.8 Hz, 1 H), 3.14 (d, J = 7.3 Hz, 2 H), 1.76 – 1.71 (m, 2 H), 1.45 – 1.37 (m, 4 H), 0.92 (d, J = 6.5 Hz, 3 H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 190.4, 146.1, 138.9, 137.8, 132.0, 126.4, 124.2, 31.0, 30.4, 28.9, 22.3, 14.0 ppm. **HRMS (EI)** calc. for [$C_{12}H_{14}ClNO_3S$]: 287.0383, found: 287.0381; **IR (neat)**: 1673 cm^{-1} (C=O); yellow oil.

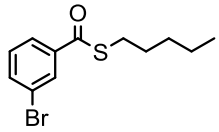


S-pentyl 2-chlorobenzothioate: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.63 (dd, J = 7.6, 1.6 Hz, 1 H), 7.38 (dtd, J = 9.7, 8.0, 1.6 Hz, 2 H), 7.31 – 7.25 (m, 1 H), 3.08 – 3.04 (m, 2 H), 1.71 – 1.65 (m, 2 H), 1.43 – 1.34 (m, 4 H), 0.90 (dd, J = 9.3, 5.0 Hz, 3 H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 192.0, 137.7, 132.0, 130.7, 129.1, 126.6, 31.0, 29.9, 29.0, 22.2, 13.9 ppm. **HRMS (EI)** calc. for [$C_{12}H_{15}ClOS$]: 242.0532, found: 242.0528; **IR (neat)**: 1675 cm^{-1} (C=O); colorless oil.

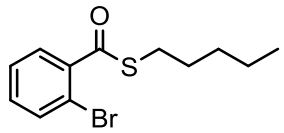


S-pentyl 2,5-dimethylbenzothioate: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.57 (s, 1 H), 7.13 (d, J = 7.6 Hz, 1 H), 7.10 – 7.04 (m, 1 H), 3.00 (td, J = 7.7, 1.5 Hz, 2 H), 2.41 (d, J = 5.1 Hz, 3 H), 2.31 (d, J = 5.2 Hz, 3 H), 1.69 – 1.62 (m, 2 H), 1.42 – 1.33 (m, 4 H), 0.91 (dd, J =

7.1, 5.6 Hz, 3 H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 194.3, 137.6, 135.2, 133.5, 132.2, 131.4, 128.8, 31.1, 29.4, 22.3, 20.8, 20.0, 13.9 ppm. **HRMS (EI)** calc. for [$C_{14}H_{20}OS$]: 236.1235, found: 236.1233; **IR (neat)**: 1678 cm^{-1} (C=O); colorless oil.

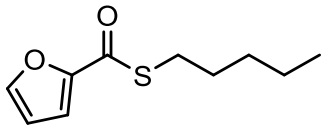


S-pentyl 3-bromobenzothioate: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.08 (t, J = 1.7 Hz, 1 H), 7.88 (ddd, J = 7.8, 1.6, 1.0 Hz, 1 H), 7.66 (ddd, J = 8.0, 2.0, 1.0 Hz, 1 H), 7.32 – 7.27 (m, 1 H), 3.05 (d, J = 7.4 Hz, 2 H), 1.69 – 1.63 (m, 2 H), 1.42 – 1.34 (m, 4 H), 0.90 (d, J = 7.2 Hz, 3 H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 190.7, 138.9, 136.0, 130.1, 125.7, 122.8, 31.1, 29.2, 22.3, 14.0 ppm. **HRMS (EI)** calc. for [$C_{12}H_{15}BrOS$]: 286.0027, found: 286.0025; **IR (neat)**: 1655 cm^{-1} (C=O); colorless oil

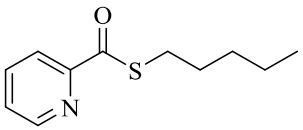


S-pentyl 2-bromobenzothioate: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.63 – 7.55 (m, 2 H), 7.36 – 7.26 (m, 2 H), 3.06 (t, J = 7.4 Hz, 2 H), 1.72 – 1.65 (m, 2 H), 1.44 – 1.33 (m, 4 H), 0.91 (t, J = 7.1 Hz, 3 H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 192.9, 139.7, 133.9, 132.0, 129.0,

127.1, 118.7, 31.0, 29.9, 29.0, 22.2, 13.9 ppm. **HRMS (EI)** calc. for [$C_{12}H_{15}BrOS$]: 286.0027, found: 286.0027; **IR (neat)**: 1672 cm^{-1} (C=O); colorless oil.

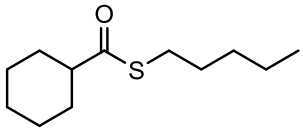


S-pentyl furan-2-carbothioate: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.57 (dd, J = 1.6, 0.8 Hz, 1 H), 7.17 (dd, J = 3.6, 0.7 Hz, 1 H), 6.55 – 6.50 (m, 1 H), 3.04 (t, J = 7.3 Hz, 2 H), 1.69 – 1.63 (m, 2 H), 1.36 (dtd, J = 7.6, 6.5, 2.2 Hz, 4 H), 0.90 (t, J = 7.1 Hz, 3 H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 180.5, 150.9, 145.8, 115.1, 112.0, 30.8, 29.2, 28.0, 22.1, 13.8 ppm. **HRMS (EI)** calc. for [$C_{10}H_{14}O_2S$]: 198.0715, found: 198.0715; **IR (neat)**: 1648 cm^{-1} (C=O); colorless oil.

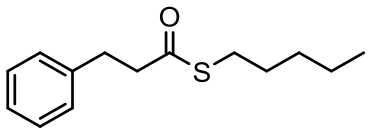


S-pentyl pyridine-2-carbothioate: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.71 – 8.67 (m, 1 H), 7.96 (dd, J = 7.8, 0.8 Hz, 1 H), 7.85 (ddd, J = 7.7, 1.6, 0.8 Hz, 1 H), 7.50 (ddd, J = 7.4, 4.8, 0.9 Hz, 1 H), 3.05 (t, J = 7.4 Hz, 2 H), 1.72 – 1.66 (m, 2 H), 1.47 – 1.33 (m, 4 H), 0.90 (t, J = 7.2 Hz, 3 H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 193.4, 151.9,

148.9, 137.0, 127.5, 120.2, 31.0, 28.9, 28.5, 22.1, 13.8 ppm. **HRMS (EI)** calc. for [$C_{11}H_{15}NOS$]: 209.0874, found: 209.0874; **IR (neat)**: 1665 cm^{-1} (C=O); colorless oil.

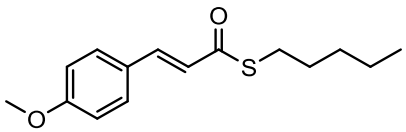


S-pentyl cyclohexanecarbothioate: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 2.88 – 2.78 (m, 2 H), 2.49 – 2.40 (m, 1 H), 1.90 (d, J = 12.1 Hz, 2 H), 1.77 (d, J = 8.5 Hz, 2 H), 1.65 (d, J = 5.2 Hz, 1 H), 1.58 – 1.52 (m, 2 H), 1.50 – 1.41 (m, 2 H), 1.39 – 1.27 (m, 5 H), 1.26 – 1.15 (m, 2 H), 0.89 (dd, J = 9.0, 4.6 Hz, 3 H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 202.7, 77.4, 77.1, 76.8, 52.6, 30.9, 29.4, 28.3, 25.5, 22.1, 13.8 ppm. **HRMS (EI)** calc. for [$C_{12}H_{22}OS$]: 214.1391, found: 214.1391; **IR (neat)**: 1687 cm^{-1} (C=O); colorless oil.

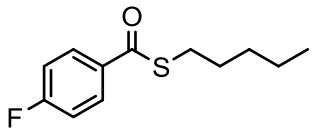


S-pentyl 3-phenylpropanethioate: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.25 (t, J = 7.6 Hz, 2H), 7.16 (t, J = 7.5 Hz, 3 H), 2.98 – 2.93 (m, 2 H), 2.87 – 2.80 (m, 4 H), 1.58 – 1.51 (m, 2 H), 1.31 (dt, J = 7.3, 5.0 Hz, 4 H), 0.89 (d, J = 6.9 Hz, 3 H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 198.4, 140.1, 128.3, 126.2, 45.4, 31.4, 30.9, 29.2, 28.8, 22.2, 13.9

ppm. **HRMS (EI)** calc. for [$C_{14}H_{20}OS$]: 236.1235, found: 236.1234; **IR (neat)**: 1687 cm^{-1} (C=O); colorless oil.

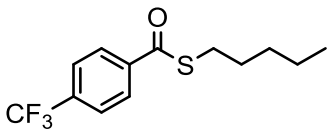


S-pentyl (E)-3-(4-methoxyphenyl)prop-2-enethioate: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.56 (d, J = 15.7 Hz, 1 H), 7.48 (d, J = 8.7 Hz, 2 H), 6.89 (d, J = 8.7 Hz, 2 H), 6.59 (d, J = 15.7 Hz, 1 H), 3.86 – 3.79 (m, 3 H), 2.99 (t, J = 7.3 Hz, 2 H), 1.65 – 1.60 (m, 2 H), 1.42 – 1.30 (m, 4 H), 0.90 (t, J = 7.0 Hz, 3 H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 189.9, 161.6, 139.9, 130.1, 126.8, 122.9, 114.4, 55.4, 31.1, 29.4, 28.9, 22.3, 14.0 ppm. **HRMS (EI)** calc. for [$C_{15}H_{20}O_2S$]: 264.1184, found: 264.1183; **IR (neat)**: 1686 cm^{-1} (C=O); colorless oil.

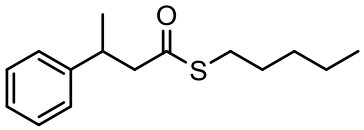


S-pentyl 4-fluorobenzothioate: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.05 (t, J = 8.5 Hz, 2 H), 7.69 (t, J = 8.7 Hz, 2 H), 3.13 – 3.05 (m, 2 H), 1.71 – 1.65 (m, 2 H), 1.42 – 1.34 (m, 4 H), 0.95 – 0.88 (m, 3 H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 190.9, 140.0, 127.5, 125.6, 31.1, 29.2, 22.2, 13.9 ppm. **HRMS (EI)** calc. for [$C_{12}H_{15}FOS$]: 226.0828,

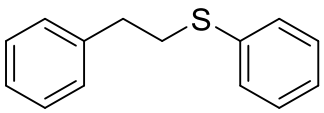
found: 226.0825; **IR (neat)**: 1660 cm^{-1} (C=O); colorless oil.



S-pentyl 4-(trifluoromethyl)benzothioate: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.98 (ddd, J = 8.9, 5.3, 2.1 Hz, 2 H), 7.09 (ddd, J = 8.9, 4.1, 2.1 Hz, 2 H), 3.09 – 3.02 (m, 2 H), 1.70 – 1.62 (m, 2 H), 1.46 – 1.33 (m, 4 H), 0.91 (dt, J = 7.2, 3.5 Hz, 3 H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 190.3, 167.0, 164.5, 133.6, 129.6, 115.7, 115.4, 31.0, 29.1, 22.2, 13.9 ppm. **HRMS (EI)** calc. for [$C_{13}H_{15}F_3OS$]: 276.0796, found: 276.0794; **IR (neat)**: 1664 cm^{-1} (C=O); colorless oil.



S-pentyl 3-phenylbutanethioate: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.26 (t, J = 7.4 Hz, 2 H), 7.22 – 7.12 (m, 3 H), 3.32 (dd, J = 14.7, 7.1 Hz, 1 H), 2.78 (dt, J = 14.7, 7.0 Hz, 4 H), 1.54 – 1.46 (m, 2 H), 1.29 – 1.25 (m, 7 H), 0.86 (t, J = 6.7 Hz, 3 H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 198.0, 145.3, 128.4, 126.7, 126.4, 52.2, 37.0, 30.8, 29.2, 28.8, 22.1, 21.4, 13.9 ppm. **HRMS (EI)** calc. for [$C_{15}H_{22}OS$]: 250.1391, found: 250.1390; **IR (neat)**: 1686 cm^{-1} (C=O); colorless oil.



Phenethyl(phenyl)sulfane: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.03 (m, 5H), 3.11 (ddd, J = 11.5, 6.8, 3.1 Hz, 1H), 2.87 (dd, J = 14.5, 7.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.06 (s), 137.30 (s), 130.01 (s), 129.81 (s), 129.31 (d, J = 14.8 Hz), 127.32 (s), 126.81 (s), 36.49 (s), 35.91 (s); colorless oil.

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국문초록

3,4-다이메틸-5-바이닐싸이아졸리움 고분자는 3,4-다이메틸-5-바이닐싸이아졸을 유리기중합을 통하여 합성한다. 이는 고분자 촉매로써 DBU와 함께 사용하여 알데하이드와 싸이올의 싸이오에스터리피케이션 실험에 사용되었고, 스타이렌과 싸이올의 싸이올-엔 순간 반응에도 사용되었다. 5-바이닐싸이아졸리움 고분자는 높은 촉매 활성도를 보였고 활성도의 저하없이 세번 이상의 재사용이 가능했다.

주요어: 고분자 촉매, 바이닐싸이아졸리움 고분자, 싸이오에스터리피케이션, 싸이올-엔 순간 반응, 고분자 재사용

학번: 2013-22940